IOP Conf. Series: Materials Science and Engineering **15** (2010) 012088 doi:10.1088/1757-899X/15/1/012088

Combined luminescence and X-ray emission study of self-trapped excitons in oxides

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Abstract. The experimental study of relaxation of anion and cation excitons at the selective VUV-(valence) and soft X-ray (inner-shell) excitations for binary BeO crystal and multicomponent oxide crystals Be_2SiO_4, $Al_2Be_3Si_6O_{18}$ and Y_2SiO_5 is presented. Results show that the relaxation during the time-scale of decay of short-living anion and cation excitations leads to creation of self-trapped excitons at the corresponding low-symmetry (tetrahedral) local structural units of crystalline lattice. This can be caused by increase of dynamical instability of such a local structural units (in comparison with high symmetry ones), which facilitates self-trapping processes in these systems.

1. Introduction

The phenomenon of self-trapping of electronic excitations (EEs) is an established mechanism of transformation of the absorbed energy in wide band gap crystals. At low temperatures this process results in the formation of anion self-trapped excitons (ASTEs), which may decay radiatively with luminescence or create defect-exciton complexes in oxides. In the binary BeO crystal the ASTE luminescence at 4.9 eV and at 6.7 eV is a result of the decay of two different ASTEs, which are distinguished by the symmetry of the hole nucleus (the O^- – ions either at the vertex or the bottom plane of the distorted oxygen tetrahedron around a central Be) [1]. At least two bands of the ASTE luminescence have previously been observed in all the crystals studied here [2-4]. The luminescence bands peaked at 3.5 eV and at 4.1 eV have earlier been interpreted as the radiative ASTE decay in Be_2SiO_4 crystals [2]. Later Zatsepin *et al.* speculated that *the creation of unrelaxed oxygen excitons result in formation of anion self-trapped excitons* in both the silicon-oxygen and the beryllium-oxygen tetrahedra [3].The 3.5 eV luminescence is a result of the radiative decay of the ASTE formed in the silicon-oxygen tetrahedra, whereas the 4.1 eV luminescence would be related to the ASTE decay within the beryllium-oxygen tetrahedra. Further, the observed 3.5 eV luminescence band is more intense than the 4.1 eV band, which indicates that the ASTE would be preferably formed within a silicon-oxygen tetrahedron. Simultaneously, the analysis of ASTE formation in Y_2SiO_5 crystals in ref. 4 reaches a conclusion that only the polyhedra containing heavy cations are involved in the self-trapping process. For the other crystals included in the present work the role of the structural crystalline units in the self-trapping process has not been discussed in literature. To the best of our knowledge there are no earlier reported experimental data for multi-component oxides that would reflect the role of the local crystal environment in the ASTE formation process.

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To contrast the limited availability of relevant ASTE investigations, there are a few reports about available, which by have studied by means of the resonant inelastic X-ray scattering (RIXS) method the formation of cation self-trapped excitons (CSTEs) in wide-gap compounds [5, 6]. First Ma *et al.* [5] observed a distinguishable side-band adjacent to the elastic scattering peak in the RIXS spectra for excitations in the vicinity of the C 1s core exciton resonance, while the absorption spectrum only showed a single sharp excitonic peak (without any side-band). The authors suggested that the origin of this RIXS side-band lies in the strong vibronic coupling that would lead to a local lattice distortion, and to the corresponding shifts in the excited electronic state. The appearance of the energy loss wing in the electronically elastic part of the RIXS spectra indicates that such distortion must have already occurred during the lifetime of the inner-shell hole. In oxide compounds a similar energy loss wing has been observed in the RIXS spectra of powder $LiNO_3$ [6], where it was attributed to the dynamics of X-ray emission, accompanying the distortion of NO_3^- species.

The present work is devoted to combined research of the ASTE and CSTE properties using the luminescence and the RIXS spectroscopies at the selective XUV excitation in several oxide crystals: BeO, Be_2SiO_4, $Al_2Be_3Si_6O_{18}$, Y_2SiO_5.

2. Experimental

The BeO, Be_2SiO_4 and $Al_2Be_3Si_6O_{18}$ crystals have been grown from a solution in a sodium tungstate melt by V. A. Maslov, G. V. Bukin and L. I. Isaenko at the Design and Technological Institute of Monocrystals in Novosibirsk, Russia and the Y_2SiO_5 crystal was grown by A. M. Korovkin using the Chokhralsky method at the Vavilov State Optical Institute in St. Petersburg, Russia.

The luminescence spectra (2.5 - 8 eV), the luminescence excitation spectra (7 – 24 eV and 50 – 200 eV) at T=10 K and at 300 K were measured at the SUPERLUMI station [7] and at the BW3 beamline using the luminescence installation described in [8], both at HASYLAB, Hamburg, Germany.

The RIXS spectra with the excitations in the vicinity of the Be 1s and the Si 2p photoabsorption edges, and the Be 1s and Si 2p photoabsorption spectra were measured at T=300 K at beamline I511-3 at MAX-lab, Lund, Sweden [9]. The resolution of the beamline monochromator (a modified SX700 by Zeiss) was set to 0.1 eV and the resolution of the X-ray spectrometer on the end station was set to 0.2 eV.

3. Results

The luminescence spectra and the luminescence excitation spectra in the vicinity of ASTE (at the fundamental absorption edge) and CSTE (near Be 1s photoabsorption edge) creation thresholds for BeO are presented in figure 1. The values of the Stokes shifts of the intrinsic luminescence bands give a measure of the energy loss during ASTE formation.

The RIXS spectra of BeO crystals at the selective excitation with the photons of different energies near Be 1s photoabsorption edge are presented in figure 2. Opposing profiles of the excitation spectra of UV-VUV luminescence and X-ray fluorescence observed in figures 1 and 2 indicate the competition between different channels of relaxation processes of electronic excitations.

In figure 2 one can see the elastic peak of RIXS spectra has an unusually strong energy loss wing at its low energy side. In our earlier works [10, 11] this observed peculiarity of the RIXS spectra was attributed to the CSTE formation. The spectral width of the energy loss wing is shown in figure 2 to estimate the energy loss for the CSTE formation. The comparison of respective values shown in figures 1 and 2 leads us to a conclusion that the energy loss for both the ASTE and the CSTE formation is approximately equal (near 5.5 - 6 eV in the case of BeO).

The results presented in figures 1 and 2 and as we have earlier discussed in detail in refs. 10 and 11, allows to propose that the self-trapping of anion and cation excitons occurs in the same local units of the crystalline lattice in oxides and that it may be caused by the predisposition of such local units to short-term transient distortion. In the present work this interpretation appears to receive corroboration

from the ASTE and CSTE comparative spectroscopic investigation from an extended variety of materials, namely from the multicomponent oxide Be_2SiO_4, $Al_2Be_3Si_6O_{18}$, Y_2SiO_5 crystals.

The luminescence spectra of the crystalline Be_2SiO_4 with excitations near the fundamental absorption edge as well as in the vicinity of core level thresholds are characterized by two intrinsic luminescence bands with maxima at 3.5 eV and at 4.1 eV (shown in figure 3). The crystalline lattice of Be_2SiO_4 contains distorted silicon-oxygen and beryllium-oxygen tetrahedra. According to the reasoning presented in ref. 3 the higher relative intensity of the 3.5 eV luminescence indicates that the ASTE formation rate is higher in the silicon-oxygen tetrahedra.

The RIXS spectra of Be_2SiO_4 excited in the vicinity of the Si 2p and the Be 1s photoabsorption edges are shown in figures 4 and 5, respectively. In both cases we were able to distinguish an energy loss wing adjacent to the elastic scattering peak. We interpret this as an indication that the CSTE can be created at both the Be- and the Si-centered tetrahedra.

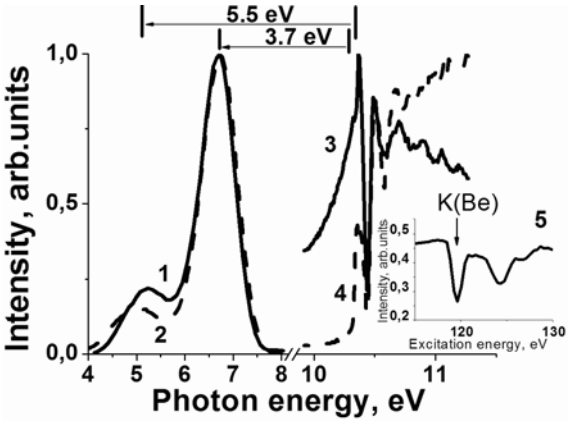

Figure 1. Photoluminescence (1, 2) and luminescence excitation (3, 4, 5) spectra of BeO crystals at T=10 K. Excitation energy: 10.8 eV (curve 1) and 119.5 eV (curve 2). Emission energy: 4.9 eV (3, 5) and 6.7 eV (4).

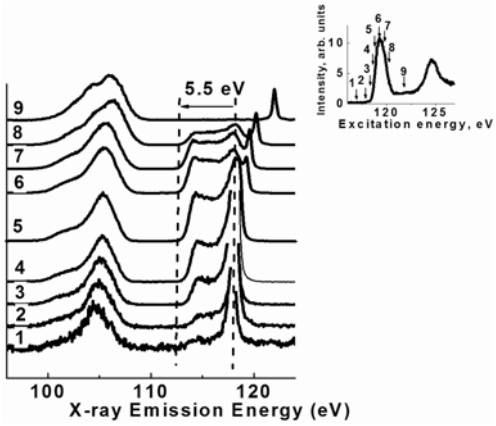

Figure 2. The X-ray emission spectra of BeO crystals excited in the vicinity of Be 1s photoabsorption edge. The numbers at the curves denote different excitation energies (see insert).

It can well be seen from the comparison of figures 4 and 5 that for the excitations near the Be_2SiO_4 Si 2p absorption edge the sub-bandgap energy loss wing is more pronounced than for excitations near the Be 1s edge. This result of our present study obtained for CSTE in their creation region provides a further support for the suggestion made in ref. 3 on the dominating role of the silicon-oxygen tetrahedra in the self-trapping processes. Additionally, we can see from the comparison of the Be_2SiO_4 luminescence (in figure 3) and the X-ray emission spectra (in figures 4 and 5) that the energy loss values for the ASTE and the CSTE formation are again approximately equal like in BeO.

As a contrast to what we observe for the Be_2SiO_4, the RIXS spectra of Y_2SiO_5 in the vicinity of the Si 2p photoabsorption edge (shown in figure 6) do not contain any detectable sub-bandgap energy loss features. This result is in good agreement with the conclusion made in ref. 4 which stated that silicon-oxygen tetrahedra do not play asignificant role in the process of ASTE formation in Y_2SiO_5.

Different from Be_2SiO_4 and Y_2SiO_5, the possible role of structural crystalline units in the process of ASTE formation has to our knowledge not been discussed for $Al_2Be_3Si_6O_{18}$ in any earlier papers. Therefore the investigation of ASTEs and CSTEs formation in this crystal is of special interest as a test case for the hypothesis that the short-term distortions, which obviously influence the creation of the self-trapped excitons, is a more general phenomenon in large band gap oxides.

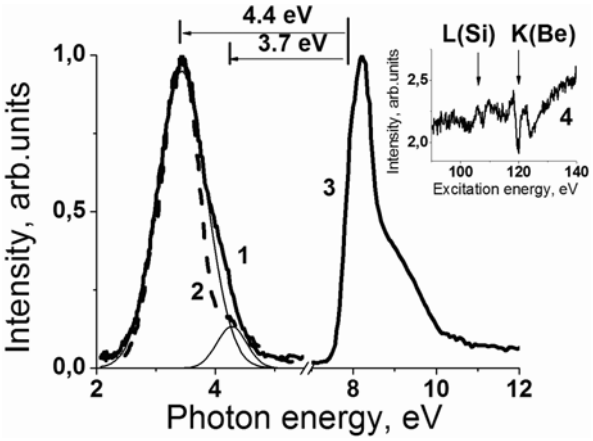

Figure 3. The photoluminescence (1, 2) and the 3.5 eV luminescence band excitation (3, 4) spectra of crystalline Be_2SiO_4 at T=10 K. The excitation energy is 8.2 eV (curve 1) and 130 eV (curve 2). The decomposition of curve 1 into Gaussian components is shown by narrow lines.

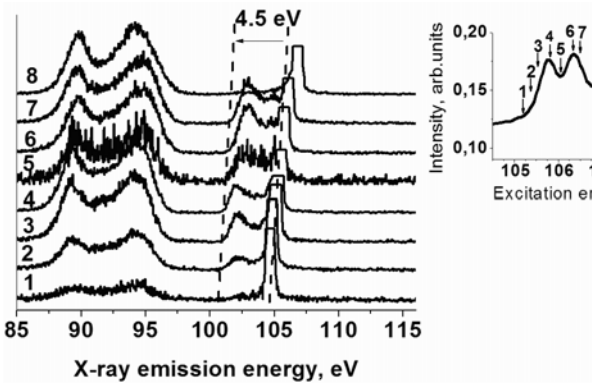

Figure 4. The X-ray emission spectra of crystalline Be_2SiO_4 excited in the vicinity of the Si 2p photoabsorption threshold. The numbers at the curves denote excitation energies as shown at the fluorescence yield curve in the inset.

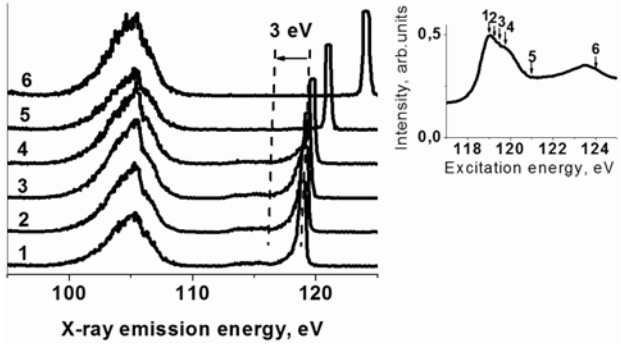

Figure 5. The X-ray emission spectra of Be_2SiO_4 crystals measured in the vicinity of Be 1s photoabsorption edge. Numbers of curves denote different excitation energies of excited photons (shown at the fluorescence excitation spectrum in the inset).

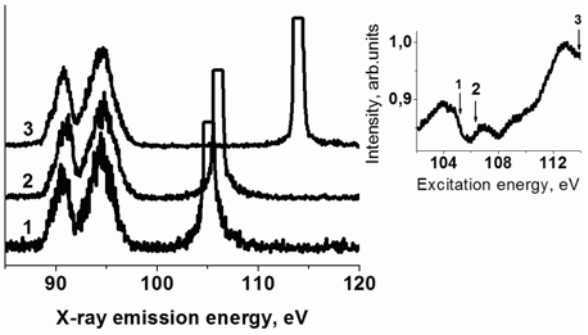

Figure 6. The X-ray emission spectra of Y_2SiO_5 crystals measured in the vicinity of Si 2p photoabsorption edge. Numbers of curves denote different excitation energies of excited photons (shown at the fluorescence excitation spectrum in the inset).

The luminescence spectra of the beryl ($Al_2Be_3Si_6O_{18}$) crystal for excitations near the fundamental absorption edge as well as for excitations in the vicinity of the Si 2p, Be 1s or O 1s core thresholds is characterized by two intrinsic bands – 3.5 and 4.9 eV (figure 7). The RIXS spectra of this crystal measured in the vicinity of Si 2p photoabsorption edge are shown in figure 8. Analogously to Be_2SiO_4 crystals we have observed energy loss wing of elastic peak in this case. However we did not register any energy loss wing of elastic peak in the RIXS spectra measured at the excitation in the vicinity of Al 2p and Be 1s photoabsorption edge.

4. Discussion

It has been established commonly that the ASTE luminescence is only observed in low-symmetry oxides. Therefore, it is exteremely important to analyse the possible creation pathways of the CSTEs, which were revelead in the crystalline $Al_2Be_3Si_6O_{18}$.

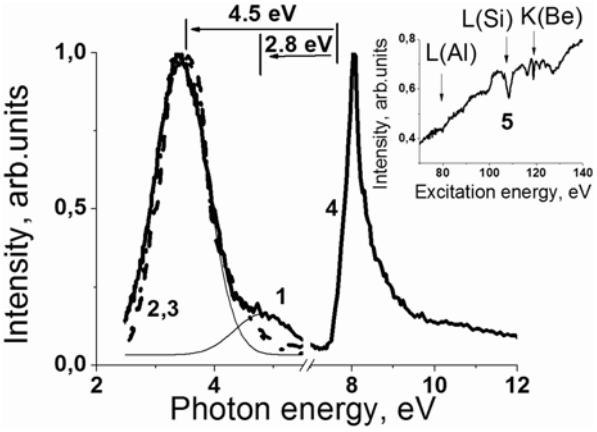

Figure 7. The photoluminescence (1-3) and the 3.5 eV luminescence band excitation (4,5) spectra of $Al_2Be_3Si_6O_{18}$ at T=10 K. The excitation energies were 8.0 eV for curve 1, 130 eV for curve 2 and 525 eV for curve 3. The thin lines show the decomposition of curve 1 into Gaussian components.

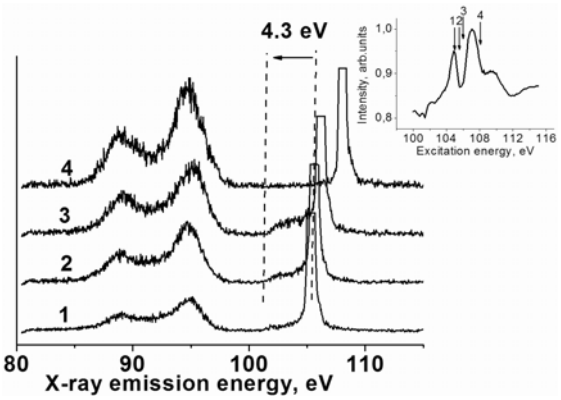

Figure 8. RIXS spectra of $Al_2Be_3Si_6O_{18}$ crystals measured in the vicinity of Si 2p photoabsorption edge. The numbers at the curves correspond to the excitation energies as shown at the fluorescence excitation spectrum in the inset. The measurements were done at T = 300K.

Namely, similar to Be_2SiO_4 crystals, the crystalline lattice of $Al_2Be_3Si_6O_{18}$ is constituted of oxygen tetrahedra, which are surrounded by Si, Be and Al ions. However, there is an essential difference between these compounds. In the Be_2SiO_4 (phenakite) crystals all the tetrahedra are distorted [12], but in the crystalline $Al_2Be_3Si_6O_{18}$ (beryl) only the silicon-oxygen tetrahedra are considerably distorted whereas lattice near the vicinity of Be and Al is geometrically quite regular [13]. As mentioned above, we do indeed observe a distinguishable sub-band gap energy loss wing next to the elastic peak in RIXS for the excitations near the Si 2p threshold of beryl, whereas for at both the Be 1s and the Al 2p excitation thresholds this wing was absent. This allows us to suggest that also the CSTE can be realized only in the low-symmetry structural units, similar to what is already known for the ASTE in oxides. However, we note that the low symmetry of the immediate neighborhood of a created electronic excitation only appears as a necessary, but not the sufficient condition for self-trapping. For example, the Y_2SiO_5 crystals also do contain the distorted silicon-oxygen tetrahedra, where the self-trapping of excitons does not occur. A possible reason for such behavior might be the existence of the weaker yttrium-oxygen bonds. Breaking of the weaker bonds is then preferred and the self-trapping of excitons is favored within yttrium-oxygen polyhedra. On the other hand, if the self-trapping of anion excitons is realized in any structural units when the CSTE will be formed on the same structural units with the specific spectroscopic features observable. In our present study this situation is typical for BeO and Be_2SiO_4. In both these cases the amount of energy loss related to the self-trapping of either the anion or the cation excitons seems to have approximately same value. Therefore, we propose that the formation of the ASTE and the CSTE in the same crystalline units should be a quite general phenomenon in low-symmetry oxide crystals.

5. Summary

A RIXS and luminescence spectroscopic study of the self-trapping of anion and cation excitons in several oxide crystals (BeO, Be_2SiO_4, $Al_2Be_3Si_6O_{18}$, Y_2SiO_5) has been carried out. Results show that the relaxation during the time-scale of decay of short-living anion and cation excitations leads to creation of self-trapped excitons at the corresponding low-symmetry (tetrahedral) local structural units of crystalline lattice. This can be caused by increase of dynamical instability of such a low symmetry (tetrahedral) local structural units (in comparison with high symmetry ones), which facilitates self-trapping processes in these systems.

Acknowledgements

This work has been partially supported by the Estonian Science Foundation grant ETF7615, the NATO grant CBP.EAP.CLG 983489 and the Russian Priority National Project "Education" (innovation educational program of the Yeltsin Ural Federal University). Synchrotron radiation studies in HASYLAB and MAX-Lab were supported by the European Comission (Grant FP7/2007-2013, grant 226716, grant 20080019) and the HASYLAB Project II-20080019.

References

[1] V. A. Pustovarov, V. Yu. Ivanov, M. Kirm, A. V. Kruzhalov, A. V. Korotaev, G.Zimmerer, *Phys. of the Solid State* **43**, 1233 (2001).
[2] V. Yu. Ivanov, V. A. Pustovarov, E.S. Shlygin , A.V.Korotaev, A. V. Kruzhalov, *Phys. of the Solid State* **47**, 466 (2005).
[3] A. F. Zatsepin, A.I.Kukharenko, V.A.Pustovarov, V.Yu. Yakovlev, S.O. Cholakh, *Phys. of the Solid State* **51**, 465 (2009).
[4] V. Yu. Ivanov, E.S.Shlygin, V.A.Pustovarov, V.V.Mazurenko, B.V.Shul'gin, *Phys. of the Solid State* **50**, 1692 (2008).
[5] Y. Ma, P. Skytt, N. Wassdahl, P. Glans, D. C. Mancini, J. Guo, J. Nordgren, *Phys. Rev. Lett.* **71**, 3725 (1993).
[6] A. B. Preobrajenski, A.S.Vinogradov, S.A.Krasnikov, R. Szargan, N. Martensson, *Phys. Rev.* **B 69**, 115116 (2004).
[7] G. Zimmerer, *Nucl. Instr. Meth. Phys. Res.* **A 308**, 178 (1991).
[8] M.Kirm, A. Lushchik, Ch. Lushchik, S. Vielhauer, G. Zimmerer, *Journ. Lumin.* **102**, 307 (2003).
[9] R. Denecke, P. Väterlein, M. Bässler, N. Wassdahl, S. Butorin, A. Nilsson, J.-E. Rubensson, J. Nordgren, N. Mårtensson, R. Nyholm, *J. Electron Spectrosc. Rel. Phenom.* **101-103**, 971 (1999).
[10] V. Pustovarov, V. Ivanov, M. Kirm, A. Kikas, K. Kooser, T. Käämbre, A.Kruzhalov, E.Zinin, *Nucl. Inst. Meth. Phys. Res.* **A 575**, 172(2007).
[11] T. Käämbre, A.Kikas, K.Kooser, V. Kisand, M. Kirm, A. Saar, E. Nommiste, V. Ivanov, V. Pustovarov, I. Martinson, *J. Electr. Spectrosc. Rel. Phenom.* **156–158**, 299 (2007).
[12] J.W. Downs, G.V. Gibbs, *American Mineralogist* **72**, 769 (1987).
[13] L. N. Solov'eva, V. V. Bakalin, *Russ. Journ. Struct. Chem.* **7**, 469 (1966).